EQUATION-OF-STATE THEORY APPLIED TO MIXTURES OF ISOTACTIC POLY(ETHYL METHACRYLATE) AND POLY(VINYLIDENE FLUORIDE)

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range of dielectric constants (3.5–35) used here. Since the calculated quantities show the same qualitative trends throughout this range of dielectric constants, we would expect our conclusions to hold when a more sophisticated electrostatic potential is employed.

Added in Proof: If bolaform electrolytes were studied at a temperature different from the Θ temperature for polymethylene, an additional perturbation would arise from the excluded-volume effect. Since the interaction of the charged chain ends becomes negligible as n becomes infinite, the expansion arising from the excluded-volume effect would dominate for large bolaform electrolytes.

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References and Notes

(1) Rice, S. A.; Nagasawa, M. "Polyelectrolyte Solutions"; Academic Press: New York, 1961.
(2) Abe, A.; Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.
(3) Patterson, G. D.; Flory, P. J. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1098.
(4) Jernigan, R. L.; Flory, P. J. *J. Chem. Phys.* **1969**, *50*, 4165.
(5) Yoon, D. Y.; Flory, P. J. *J. Chem. Phys.* **1974**, *61*, 5366.
(6) Jernigan, R. L.; Flory, P. J. *J. Chem. Phys.* **1969**, *50*, 4178.
(7) Mattice, W. L.; Napper, D. H. *Macromolecules*, in press.
(8) Feigin, R. I.; Napper, D. H. *J. Colloid Interface Sci.* **1979**, *71*, 117.
(9) Smith, R. P. *J. Chem. Phys.* **1965**, *42*, 1162.
(10) Mattice, W. L.; Santiago, G. *Macromolecules* **1980**, *13*, 1560.
(11) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 303.
(12) Solc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1971**, *54*, 2756.
(13) Solc, K. *J. Chem. Phys.* **1971**, *55*, 355.
(14) Kranbuehl, D. E.; Verdier, P. H. *J. Chem. Phys.* **1977**, *67*, 361.
(15) Mattice, W. L. *Macromolecules* **1979**, *12*, 944.
(16) Mattice, W. L. *J. Am. Chem. Soc.* **1980**, *102*, 2242.
(17) Mattice, W. L. *Macromolecules* **1980**, *13*, 506.
(18) Mattice, W. L. *Macromolecules* **1980**, *13*, 904.
(19) Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *6*, 506.
(20) Stratton, J. A. "Electromagnetic Theory"; McGraw-Hill: New York, 1941.
(21) Westheimer, F. H.; Kirkwood, J. G. *J. Chem. Phys.* **1938**, *6*, 513.
(22) Skolnick, J.; Fixman, M. *Macromolecules* **1978**, *11*, 867.

Equation-of-State Theory Applied to Mixtures of Isotactic Poly(ethyl methacrylate) and Poly(vinylidene fluoride)

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ABSTRACT: Flory's equation-of-state theory is applied to a PVF_2/it-PEMA system with a lower critical solution temperature. A comparison is made between the observed irregular asymmetric cloud point curve and the calculated spinodals. The agreement is good for values of the mixing parameters, which are in accordance with melting point depression data.

Introduction

Over the years it has become clear that nearly all blends of miscible polymers show lower critical solution temperature (LCST) behavior. To study this, one needs polymer pairs with cloud point curves in a temperature range accessible to measurements. In this respect, the various poly(vinylidene fluoride) (PVF_2)/poly(alkyl methacrylate) systems obviously offer good prospects. In addition to the fact that many of these systems are miscible, one has the disposal of at least three parameters which affect this miscibility: the ester group, the tacticity, and the molar mass.[1-6] By a suitable adaptation of these parameters, blends with the desired properties can be obtained. A nice example, considered in this paper, is PVF_2 with low molar mass isotactic poly(ethyl methacrylate) (it-PEMA).

It is well-known that thermodynamic miscibility is only possible if the Gibbs free energy of mixing, ΔG_m, is negative, but even in that case the stability is determined by the curvature of ΔG_m as a function of composition. A strictly binary system is stable if $(\partial^2 \Delta G_m/\partial \varphi_2^2)_{P,T}$ is positive over the entire composition range. So, $\Delta G_m < 0$ is a necessary but insufficient condition for polymer–polymer miscibility. A ripple in the $\Delta G_m(\varphi_2)$ curve makes a one-phase system unstable with respect to a two-phase system and partial miscibility is the result. In that case, the points of common tangency to the $\Delta G_m(\varphi_2)$ curve define the compositions of the coexisting phases (binodal) in a temperature–composition plot.

In addition there are two inflection points in the $\Delta G_m(\varphi_2)$ curve, where in between the curvature $(\partial^2 \Delta G_m/\partial \varphi_2^2)_{P,T}$ is negative and the system is unstable. The limit of stability, also called the spinodal, is given by

$$(\partial^2 \Delta G_m/\partial \varphi_2^2)_{P,T} = 0 \quad (1)$$

In between the spinodal and the binodal $(\partial^2 \Delta G_m/\partial \varphi_2^2)_{P,T}$ is positive, but the system is metastable because the mixture is stable toward small composition changes but unstable toward sufficiently large fluctuations. Usually, a cloud point curve (CPC) is measured, which lies in between the binodal and the spinodal. If the ripple in the $\Delta G_m(\varphi_2)$ curve disappears at decreasing temperature, an LCST will be the outcome.

Several theories have been developed to explain the LCST behavior in polymer systems. The best known examples are Flory's equation-of-state theory and the lattice fluid theory.[7,8] All these approaches adopt the classical Flory–Huggins expression for the combinatorial entropy of mixing. As a result of this contribution to the Gibbs free energy of mixing, the calculated binodals and spinodals are shifted toward the region of compositions poor in the constituent with the larger average chain length.

A cloud point curve which is characteristic for blends of low molar mass it-PEMA and PVF_2 is shown in Figure 1. The miscibility gap for these blends is located in the PVF_2-rich region of the phase diagram; the PVF_2 molecules, however, have the larger average chain length (cf.

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Table I
Pure-Component Properties at 180 °C[a] (See Ref 15)

polymer	$\bar{M}_w$	$\alpha \times 10^3$, K^{-1}	γ, cal/(cm³·K)	v_{sp}, cm³/g	v_{sp}*, cm³/g	T*, K	P*, cal/cm³
it-PEMA	4 000	0.645	0.250	0.981	0.789	8038	175
PVF_2	100 000	0.761	0.190	0.666	0.520	7364	141

[a] It should be noted that the numbering of the two polymers is the reverse of that of ref 15.

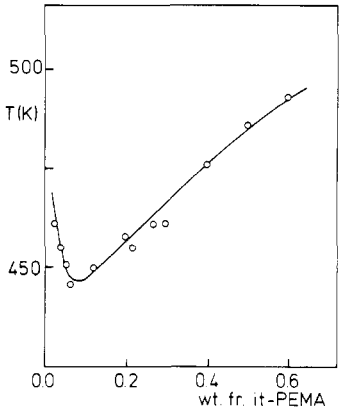

Figure 1. Cloud point curve of blends of PVF_2 with low molar mass it-PEMA recorded by turbidimetry.

Table I). This remarkable skewness of the cloud point curve is referred to as an *irregular asymmetry*.[9] It has furthermore been demonstrated that the melting point depression of PVF_2 by it-PEMA is practically zero.[10] We will show that both phenomena can be explained by a modified form of Flory's equation-of-state theory.

The Flory theory[7] is based on an assumption first made by Prigogine[11] that the degrees of freedom of a molecule in a liquid can be separated into internal and external degrees of freedom. The external degrees of freedom depend only on intermolecular interactions and are considered to be equivalent to translational degrees of freedom, whereas the internal degrees of freedom depend only on valency forces. The number of external degrees of freedom attributable to a segment in a chain molecule is less than that for a similar small molecule. Generally $3c$ ($c < 1$) is used to denote the number of external degrees of freedom per segment. Flory assumed that the intersegmental energy arises from interactions between the surfaces of adjoining segments. The mean intermolecular energy is supposed to be of the van der Waals form, that is, an energy inversely proportional to volume. Using these assumptions, Flory formulated a partition function for a mixture of N r-mers, from which the following equation of state can be derived:

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/\tilde{v}\tilde{T} \quad (2)$$

where $\tilde{P} = P/P^*$, $\tilde{v} = v/v^*$, and $\tilde{T} = T/T^*$. The hard-core volume per segment v^*, the characteristic pressure P^*, and the characteristic temperature T^* can be calculated from measurements of the thermal expansion coefficient α, the volume per segment v, and the thermal pressure coefficient γ. The relations are given by

$$\tilde{v} = v/v^* = [1 + \alpha T/3(1 + \alpha T)]^3 \quad (3)$$

$$\tilde{T} = T/T^* = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \quad (4)$$

$$P^* = \gamma T \tilde{v}^2 \quad (5)$$

The adaptation of this theory to mixtures of N_1 r_1-mers and N_2 r_2-mers is based on the assumption of random mixing of the different segments, which have to be chosen in such a way as to have equal hard-core volume. An exchange energy parameter X_{12} is introduced, which arises from considering the difference in interaction energy between like and unlike segmental pairs. Eichinger and Flory[12] also added an entropic correction parameter Q_{12} to the theory to obtain a better agreement between theory and experiment. Finally Lin[13] introduced a parameter c_{12} which characterizes the deviation from additivity of the number of external degrees of freedom per segment in the mixture. The equation of state for the two-component mixture has a form identical with that for the pure components if the following definitions are made:

$$P^* = \varphi_1 P_1^* + \varphi_2 P_2^* - \varphi_1 \theta_2 X_{12} \quad (6)$$

$$\tilde{T} = T/T^* = (1/P^*)[\varphi_1 \tilde{T}_1 P_1^* + \varphi_2 \tilde{T}_2 P_2^* - (c_{12}\varphi_1\varphi_2 kT/v^*)] \quad (7)$$

where φ_1 and φ_2 denote the segment fraction of components 1 and 2, respectively, and θ_2 is the surface fraction of component 2. On the basis of the modified Flory theory McMaster[14] derived, among other things, an expression for the spinodal of a mixture of two polymers, a simplified version of which will be applied in this study.

Results and Discussion

As mentioned before, one of the striking features of the cloud point curve for blends of low molar mass it-PEMA and high molar mass PVF_2 is the occurrence of the minimum at the PVF_2-rich side of the phase diagram. To describe this irregular asymmetry theoretically we use the modified form of Flory's equation-of-state theory, as given by McMaster,[14] without the empirical entropic correction term characterized by Q_{12}. In the low-pressure approximation, which is valid for atmospheric pressure, the expression for the spinodal is given by

$$\begin{aligned} 1/r_1\varphi_1 + 1/r_2\varphi_2 - 6 \ln (m_1/m_2)^{1/2}(c_1 - c_2) + \\ 6 \ln (m_1/m_2)^{1/2} c_{12}(\varphi_2 - 2\varphi_1) - \\ 6c_{12} \ln \{[(2\pi m_2 kT)^{1/2}/h](\gamma v^*)^{1/3}(\tilde{v}^{1/3} - 1)\} - \\ (2v^*/kT)(s_2/s)^2(s_1/s)(X_{12}/\tilde{v}) - \\ (\partial\tilde{v}/\partial\varphi_1)_{P,T}\{[c_1 - c_2 + (\varphi_1 - \varphi_2)c_{12}]/\tilde{v}^{2/3}(\tilde{v}^{1/3} - 1) - \\ (v^*/kT\tilde{v}^2)[P_1^* - P_2^* - (s_2/s)(\varphi_2 - \theta_1)X_{12}]\} = 0 \end{aligned} \quad (8)$$

This expression depends on the characteristic parameters of the pure components, reported before and collected in Table I, and on three mixture parameters: the segmental surface area ratio s_1/s_2, the exchange energy parameter X_{12}, and c_{12}, determining the deviation from additivity of the number of external degrees of freedom. The correct values of these quantities are not so easy to predict.

Olabisi's[16] results imply that the equation-of-state theory can explain the observed irregular asymmetry provided $X_{12} < 0$ and $s_1/s_2 < 1$. According to Flory,[7] s_1 and s_2 can be defined as the ratio of the area per monomeric unit and the corresponding hard-core volume. The PVF_2 molecule can be considered as a cylinder with a radius of 2.65 Å, estimated from crystallographic data of the most compact I (β) modification and the specific hard-core volume v_{sp}* of Table I. For it-PEMA, however, no crystallographic data are available. If one assumes a structure analogous to it-PMMA, a value of 4.8 Å for the radius is found. In

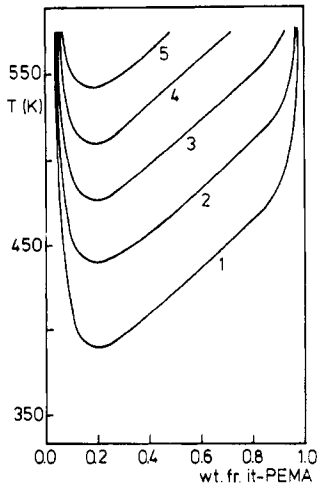

Figure 2. Simulated spinodals for it-PEMA/PVF_2 mixtures ($m_1/m_2 = 0.66$, $s_1/s_2 = 1$, $c_{12} = 0.02$): curve 1, $X_{12} = -0.5$; curve 2, $X_{12} = -1.0$; curve 3, $X_{12} = -1.5$; curve 4, $X_{12} = -2.0$; curve 5, $X_{12} = -2.5$ cal/cm^3.

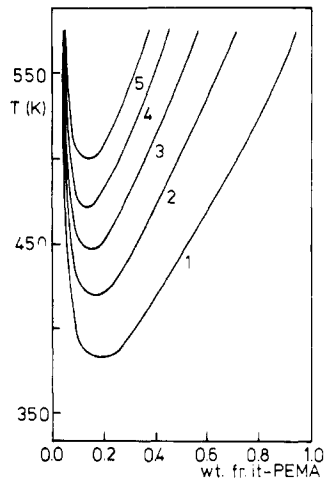

Figure 3. Simulated spinodals for it-PEMA/PVF_2 mixtures ($m_1/m_2 = 0.66$, $s_1/s_2 = 0.55$, $c_{12} = 0.02$): curve 1, $X_{12} = -0.5$; curve 2, $X_{12} = -1.0$; curve 3, $X_{12} = -1.5$; curve 4, $X_{12} = -2.0$; curve 5, $X_{12} = -2.5$ cal/cm^3.

this way s_1/s_2 equals 0.55. A negative value of X_{12} implies specific interactions between the two components, which is expected to be true for it-PEMA and PVF_2.[3] The above-mentioned criteria are therefore satisfied.

However, these conditions are not the only possibilities for the occurrence of an irregular asymmetry. A closer inspection of expression 8 shows that it can also be the result of the combination $c_{12} > 0$ and $m_1/m_2 < 1$, where m_1 and m_2 denote the mass per segment of components 1 and 2. As these segments have equal hard-core volume, the data of Table I imply that the latter condition is fulfilled, because $m_1/m_2 = v_{sp,2}^*/v_{sp,1}^* = 0.66$. The number of external degrees of freedom per segment in the mixture, $3c$, is determined by

$$c = \varphi_1 c_1 + (1 - \varphi_1)c_2 - \varphi_1(1 - \varphi_1)c_{12} \qquad (9)$$

where $3c_1$ and $3c_2$ are the external degrees of freedom per segment of the pure components and φ_1 is the segment fraction of component 1 in the mixture. Generally, specific interactions imply volume contraction on mixing. Therefore, the molecules come closer together in the mixture and the number of external degrees of freedom will be smaller than that obtained by a linear combination of the values for both pure components.[17,18] Hence $c_{12} > 0$ and $m_1/m_2 < 1$ seem also to be valid for our system.

To illustrate the asymmetric effect of c_{12}, various spinodals for $c_{12} > 0$ and $s_1/s_2 = 1$ have been generated. s_1/s_2 was chosen to be 1 in order to exclude the effect of this parameter on the skewness. Figure 2 presents spinodals for $c_{12} = 0.02$ and different values of X_{12}. The predicted irregular asymmetry is clearly demonstrated. We emphasize that the spinodals calculated for any negative value of X_{12} together with $s_1/s_2 = 1$ and $c_{12} = 0$ lie far above the observed cloud point curve and have a minimum at the it-PEMA-rich side of the phase diagram. This implies that we need a positive c_{12} in order to get a minimum of the spinodal in the proper temperature range. Moreover, this positive c_{12} contributes to the irregular location of the spinodal.

According to the foregoing analysis, the particular skewness of the CPC for the it-PEMA/PVF_2 system is due to two different combinations of factors: (i) $X_{12} < 0$ and $s_1/s_2 < 1$; (ii) $c_{12} > 0$ and $m_1/m_2 < 1$. With this in mind we have generated many spinodals for $m_1/m_2 = 0.66$, $s_1/s_2 = 0.55$, and different values of X_{12} and c_{12}. The best results, compared to the experimental cloud point curve, are obtained by taking c_{12} about 0.02. This deviation from additivity is of the same order of magnitude as found by Hamada et al.[18] for a number of poly(dimethylsiloxane)–solvent systems. Figure 3 shows the effect of the exchange energy parameter on the simulated spinodals with c_{12} kept at 0.02. A value of −1.5 cal/cm^3 seems to fit well with Figure 1.

It should be compared with the estimation of the interaction strength based upon melting point depression measurements. In this way Kwei et al.[19] and Imken et al.[20] found a slightly greater interaction density in blends of at-PEMA and PVF_2. However, it has recently been demonstrated by using the so-called Hoffman–Weeks analysis that the thermodynamic melting point depression of PVF_2 by it-PEMA is practically zero.[10] SAXS measurements supported the idea that the observed melting point depressions were entirely due to morphological effects. As a result of this the Flory–Huggins parameter χ_{12} is also approximately zero.[21] The relation between χ_{12} and X_{12} is obtained by equating the expression for the chemical potential of the Flory–Huggins theory and the equation-of-state theory.[14] Applying the low-pressure approximation gives

$$\chi_{12} = 3 \ln (m_1/m_2)^{1/2}(c_1 - c_2 + 2\varphi_1 c_{12}) + 3c_{12} \ln \{[(2\pi m_2 kT)^{1/2}/h](\gamma v^*)^{1/3}(\tilde{v}^{1/3} - 1)\} + (3c_1/\varphi_2^2) \ln \{(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)\} + (v^*/kT\varphi_2^2)[P_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + \theta_2^2(X_{12}/\tilde{v})] \qquad (10)$$

Using this expression, we have calculated χ_{12} as a function of the weight fraction it-PEMA at the temperature $T = 453$ K, for which the pure-component properties are known. The results for $s_1/s_2 = 0.55$, $c_{12} = 0.02$, and different values of X_{12} are presented in Figure 4. This figure shows that for $X_{12} = -1.5$ cal/cm^3, χ_{12} varies between 0.018 and −0.020 for weight fractions of it-PEMA below 33%. Still less negative values for χ_{12} are obtained by taking s_1/s_2 larger than 0.55. In that case, the spinodals are also flattened somewhat (cf. Figures 2 and 3). In any case these calculations clearly demonstrate that a rather negative value of the exchange energy parameter may correspond with an approximately zero value of the Flory–Huggins parameter.

To sum up, we see that reasonable agreement between theory and experiment can be obtained for the following values of the mixing parameters: $X_{12} \sim -1.5$ cal/cm^3, $c_{12} \sim 0.02$, and $s_1/s_2 \sim 0.55$. Increasing the molar mass of it-PEMA to 100 000 leads, with these mixture parameters,

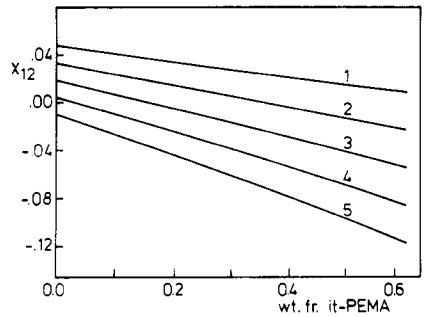

Figure 4. Flory–Huggins parameter vs. weight fraction of it-PEMA ($m_1/m_2 = 0.66$, $s_1/s_2 = 0.55$, $c_{12} = 0.02$): curve 1, $X_{12} = -0.5$; curve 2, $X_{12} = -1.0$; curve 3, $X_{12} = -1.5$; curve 4, $X_{12} = -2.0$; curve 5, $X_{12} = -2.5$ cal/cm^3.

to a calculated LCST at about 80 °C. This is, in accordance with earlier experimental observations,[6] far below the crystallization temperatures of PVF_2 in blends with it-PEMA.

As far as we know, the it-PEMA/PVF_2 system is the first polymer/polymer system exhibiting LCST behavior combined with an irregular asymmetry of the critical concentration. Mixtures of polyisobutylene ($\bar{M}_w = 250$) and poly(dimethylsiloxane) ($\bar{M}_w = 850$ and 1350) show upper critical solution temperature (UCST) behavior with an irregular asymmetric cloud point curve.[22] According to the results of Hamada et al.,[18] one should expect a positive c_{12} for this system. As the ratio of the masses per segment also satisfies $m_{PIB}/m_{PDMS} < 1$, it is tempting to attribute the observed skewness to the nonadditivity of the number of external degrees of freedom (cf. ref 9).

Conclusions

In this work we show that Flory's equation-of-state theory can reproduce the observed irregular asymmetry of the cloud point curve for blends of it-PEMA and PVF_2. The values of the mixing parameters necessary to obtain agreement between the experimental cloud point curve and the theoretical spinodal are in accordance with the observed absence of melting point depression. Moreover, the importance of the nonadditivity of the number of external degrees of freedom with respect to the skewness is demonstrated.

References and Notes

(1) Noland, J. S.; Hsu, N. N. C.; Saxon, R.; Schmitt, J. M. *Adv. Chem. Ser.* **1971**, *No. 99*, 15.
(2) Paul, D. R.; Altamirano, J. O. *Adv. Chem. Ser.* **1975**, *No. 142*, 371.
(3) Paul, D. R.; Barlow, J. W.; Bernstein, R. E.; Wahrmund, D. C. *Polym. Eng. Sci.* **1978**, *18*, 1225.
(4) Roerdink, E.; Challa, G. *Polymer* **1978**, *19*, 173.
(5) Roerdink, E.; Challa, G. *Polymer* **1980**, *21*, 509.
(6) Roerdink, E.; Challa, G. *Polymer* **1980**, *21*, 1161.
(7) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(8) Lacombe, R. H.; Sanchez, I. C. *J. Phys. Chem.* **1976**, *80*, 2568.
(9) Koningsveld, R.; Kleintjens, L. A.; Schoffeleers, H. M. *Pure Appl. Chem.* **1974**, *39*, 1.
(10) Eshuis, A.; Roerdink, E.; Challa, G., to be published in *Polymer*.
(11) Prigogine, I. "The Molecular Theory of Solutions"; North-Holland Publishing Co.: Amsterdam, 1957.
(12) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2035, 2053, 2061, 2066.
(13) Lin, P. H. Sc.D. Thesis, Washington University, St. Louis, Mo., 1970.
(14) McMaster, L. P. *Macromolecules* **1973**, *6*, 760.
(15) ten Brinke, G.; Roerdink, E.; Challa, G., to be published in *MMI Press Symp. Ser.* (Vol. 3).
(16) Olabisi, O. *Macromolecules* **1975**, *8*, 316.
(17) Kubota, K.; Kim, Y. B.; Kubo, K.; Ogino, K. *Rep. Prog. Polym. Jpn.* **1977**, *20*, 43.
(18) Hamada, F.; Shiomi, T.; Fujisawa, K.; Nakajima, A. *Macromolecules* **1980**, *13*, 729.
(19) Kwei, T. K.; Patterson, G. D.; Wang, T. T. *Macromolecules* **1976**, *9*, 780.
(20) Imken, R. L.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1976**, *16*, 593.
(21) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
(22) Allen, G.; Gee, G.; Nicholson, J. P. *Polymer* **1961**, *2*, 8.

Reviews

Polyquinolines

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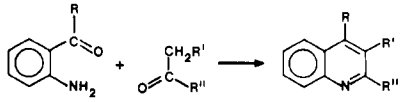
ABSTRACT: A review of the preparation and structure/property relationships of various polyquinolines is presented. The monomer and polymer syntheses and the kinetics, solution properties, morphology, thermal analyses, and cross-linking reactions of polyquinolines are discussed.

Introduction

The Friedländer reaction[1] is a base-catalyzed condensation of an *o*-amino aromatic aldehyde or ketone with a ketomethylene compound that produces a quinoline, usually in good yields. Although the reaction can be considered to be an aldol reaction followed by Schiff base formation at nitrogen or, alternatively, the reverse reaction sequence,[2,3] neither type of intermediate has been isolated, indicating that the second, cyclization step must be fast compared to the first reaction.



This type of base-catalyzed reaction has been applied to the synthesis of anthrazolines to obtain totally aromatic polymers.[4] The reaction of 4,6-diaminoisophthalaldehyde and a series of diacetyl aromatics in hexamethylphosphoric triamide gave a series of low molecular weight polyanthrazolines. Although these polymers showed reasonably

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